Pergamon

Electrochimica Acta, Vol. 41, No. 14, pp. 2321–2327, 1996

0013-4686/96 $15.00 + 0.00

PII:S0013-4686(96)00062-X

THEORY OF ION-TRANSFER KINETICS AT A VISCOUS IMMISCIBLE LIQUID/LIQUID INTERFACE BY MEANS OF THE LANGEVIN EQUATION

K. AOKI

Department of Applied Physics, Fukui University, 9-1, Bunkyo 3-chome, Fukui-shi, 910 Japan

(*Received* 30 *March* 1995; *in revised form* 2 *June* 1995)

Abstract—In the ion-transfer kinetic model at the immiscible liquid/liquid interface presented here, the transfer of an ion is controlled by an activation energy and velocity of the ion in the viscous interface. The model was enlightened by the insufficient agreement of the potential dependence of the experimental transfer coefficient with the Butler equation and by a loss of a reasonable physical meaning in the activationless kinetic theory based on the Nernst–Planck equation. The velocity of the large spherical ion in this model was driven by the desolvation energy, the energy of overcoming the interfacial tension between the two liquids, the electrostatic energy in the double layer, and the thermal fluctuation. It is retarded by the viscous force, as expressed by the Langevin equation. The activation energy resulted from the first three energies. The kinetic equation was derived from the expressions for the velocity and the activation energy through the Boltzmann's distribution equation. It could elucidate both properties of the activation control and of the viscous control. The equilibrium condition did not lead to the Nernst equation because the frictional energy should be compensated with the potential difference between the two phases. The logarithmic forward rate constant was approximately linear with the potential difference. However, the theory could not explain quantitatively the non-linearity observed experimentally for small non-spherical anions. Copyright © 1996 Elsevier Science Ltd

Key words: ion transfer kinetics, immiscible liquid/liquid interface, Langevin equation, activation energy by desolvation.

INTRODUCTION

Ion transfer across an immiscible solution interface is detected as a flow of the ion or a current driven by applied potential[1, 2]. The current-potential relation characterizes the kinetics of the ion-transfer. It has been elucidated by combination[3–8] of the interfacial ionic equilibrium or the interfacial kinetics with mass transport, as has been done in the analysis of the convectional solution/electrode interface. A typical kinetic equation is the Butler–Volmer relationship[9], of which rate-determining step is to overcome an activation energy hill, as comprehended by the absolute rate theory. Several experimental data have supported the concept of the interfacial activation energy[10–16]. However, a question has been proposed on the dependence of the transfer coefficient on the electrode potential[17–19]. The Butler–Volmer equation should be corrected for a detailed kinetic analysis or a new kinetic theory is expected to be developed.

A model opposing the Butler–Volmer equation is a rate-determining step of a frictional force in a highly viscous interfacial domain, called Goldman-type theory[18, 20]. Since this model is based on the Nernst–Planck equation[21] with a linear potential variation in the double layer, the potential energy level across the interface varies monotonically without any hill. The model predicts[18] that the charge transfer coefficient varies non-linearly with the electrode potential and that the coefficient is strictly 1/2 at the standard electrode potential. These predictions explain success fully the experimental results[18–20, 22]. The other conclusion of the theory is linear dependence of the forward rate on the potential difference when the two phases are far from the equilibrium. The dependence is essentially the same as Ohm's law. This is, however, inconsistent with the ordinary kinetic rule that reaction rates vary exponentially with an external energy.

In brief, there are two kinetic models, one being the activated Butler–Volmer type and the other being the transport type. Since both models are different in the rate-determining steps, they are basically incompatible. It is expected that exploration of a feature common to both models yields a new compatible model. The frictional force alters a momentum of the ion whereas the activation energy is relevant to the electric potential energy. The concept of the frictional force is not alternative to or not inconsistent with that of the activation energy. Indeed, it is possible to consider the viscous interfacial domain that has a high activation energy hill. The relation between the momentum and the friction can be described by the Langevin equation[23] in the light of the thermal fluctuation which contributes to overcoming the activation energy hill. This paper is devoted to the derivation of the ion-transfer

kinetic equation at the viscous liquid/liquid interface by combining the Langevin equation with the kinetic equation based on the Boltzmann's statistics in order to coordinate the Goldman-type rate theory with the Butler–Volmer equation.

MODEL AND FORMULATION

We formulate the ion-transfer kinetic equation of the Butler–Volmer type at the immiscible liquid/liquid interface from a statistical mechanical viewpoint. Let H be the x-component of the Hamiltonian of the transferring ion, where x is the directional coordinate from phase 1 (water) toward phase 2 (oil). Then the probability of taking a state of H is proportional to $\exp(-H/k_B T)$, where k_B is the Boltzmann constant. We define the interfacial activation energy U_A as a barrier of prohibiting the ion-transfer for $H < U_A$ and as a free pass for $H > U_A$. When the ion transverses the interface at velocity v, the restriction of H by U_A can be realized by setting v to zero for $H < U_A$ and by taking no limitation for $H > U_A$. Although the velocity depends on x within the thickness w of the interface, it is the average velocity that can be observed. Then the expectation of the velocity is the average over U and x, given by

$$k \equiv \int_0^\infty \int_{-w/2}^{w/2} v \, dx \exp\left(\frac{-H}{k_B T} dU\right) \times \int_0^\infty \int_{-w/2}^{w/2} dx \exp\left(\frac{-H}{k_B T}\right) dU = \int_{U_A}^\infty \int_{-w/2}^{w/2} v \, dx \exp\left(\frac{-H}{k_B T}\right) dU \times w \int_0^\infty \exp\left(\frac{-H}{k_B T}\right) dU \quad (1)$$

If H includes no kinetic energy or is equivalent to the potential energy U and if v is independent of U, the integration simplifies to

$$k = v \exp\left(\frac{-U_A}{k_B T}\right) \quad (2)$$

The energy of ions generally consists of an electric contribution and a non-electric contribution as in the solvation energy under the equilibrium condition[24, 25]. This may also be the case for the activation energy, as will be described in the following second paragraph. The electric term is a product of the charge of the ion ze (z = the charge number) by the electric potential ϕ. Difference in the potential of phase 1, ϕ_1, and of phase 2, ϕ_2, occurs only in the interfacial domain. Separation of the liquid/liquid interface into the inner layer and the diffuse double layer is ambiguous. However, it is reasonable to consider that a layer with the highest electric field controls the transfer rate. It is assumed that ϕ within the interface varies linearly with x, according to the Goldman equation[26]. This may correspond to neglecting the electric field in the diffuse double layer. Since the potential gradient depends on dielectric properties of solvents 1 and 2, it does not partition equivalently to the two phases. Let the weighting factor be α, as shown in Fig. 1. Then the electric potential energy is given by

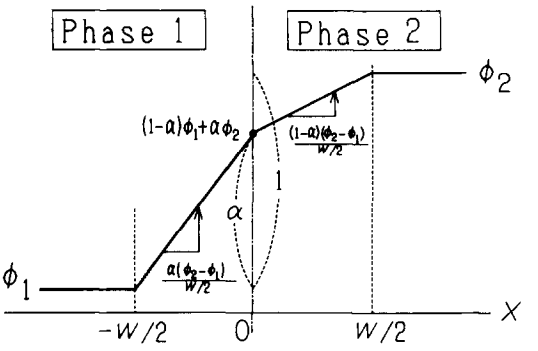

Fig. 1. The predicted profile of the electric potential at the interface.

$$U_{e-} = \left\{2(1-\alpha)(\phi_2 - \phi_1)\frac{x}{w} + (1-\alpha)\phi_1 + \alpha\phi_2\right\} ze \quad \text{for } 0 < x < w/2 \quad (3)$$

$$U_{e+} = \left\{2\alpha(\phi_2 - \phi_1)\frac{x}{w} + (1-\alpha)\phi_1 + \alpha\phi_2\right\} ze \quad \text{for } -w/2 < x < 0 \quad (4)$$

Contributions to the activation energy are $\phi_{x=0} - \phi_2$ and $\phi_{x=0} - \phi_1$,

$$U_{Ae-} = -(1-\alpha)ze(\phi_2 - \phi_1) \quad \text{for } 0 < x < w/2 \quad (5)$$

$$U_{Ae+} = \alpha ze(\phi_2 - \phi_1) \quad \text{for } -w/2 < x < 0 \quad (6)$$

On the other hand, the non-electric contributions considered here are a change in the solvation energy U_s of transferring ion and a change in the energy U_γ of making a pore of the ion-size against the interfacial tension between the two phases. Since they are short-range interactions, they may be proportional to the surface area of the ion. It is assumed that the ion is a sphere with the radius a and is larger than solvent molecules. When the centre of the ion is at position x as depicted in Fig. 2, the surface area of the sphere invading in phase 2 is expressed by

$$S_2 = \int_0^\theta 2\pi a \sin\theta \, d\theta = 2\pi a^2\left(1 + \frac{x}{a}\right) \quad (7)$$

Similarly, the surface area invading in phase 1 is $S_1 = 2\pi a^2(1 - x/a)$.

The transfer brings about replacement of the solvents. The replacement begins at temporal desolvation and then resolvation by the other solvents, as illustrated in Fig. 2 (lower part). Then a condition around the transferring ion varies gradually with x. This concept is similar to the gradual variation of solvation energy in a mixed solvent region[6]. This may be equivalent to the continuous variation of the interfacial composition which has been predicted from the molecular dynamics[27]. Let the energy density of the solvation by solvent i(i = 1, 2) be u_i

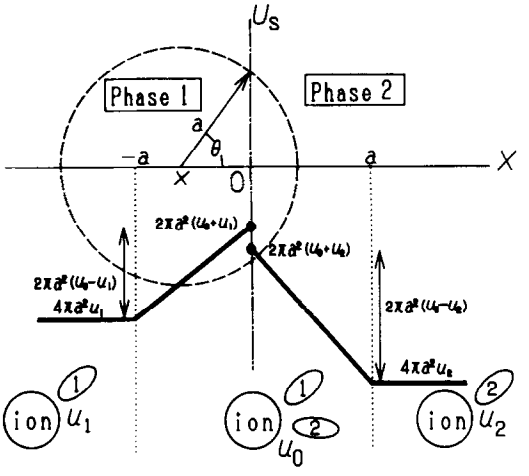

Fig. 2. The profile of the solvation energy, and illustration (lower part) of the solvation and the desolvation.

and let the energy density when both solvents are simultaneously removed be u_0 (see Fig. 2). The significance of the energy density has been demonstrated by the linearity of the solvation energies with surface areas of various ions[25]. For the forward transfer or the positive movement from $-a$, the rate-determining step is to remove solvent 1 to reach the intermediate state in which the ion shares solvents 1 and 2 at a common solvation site. Then the activation profile for the forward transfer is expressed by

$$U_{s+} = (u_0 - u_1)S_2 = 2\pi a^2(1 + x/a)(u_0 - u_1) \quad \text{for } -a < x < 0 \quad (8)$$

Similarly, the ion experiences the energy hill for the negative transfer, given by

$$U_{s-} = (u_0 - u_2)S_1 = 2\pi a^2(1 - x/a)(u_0 - u_2) \quad \text{for } 0 < x < a \quad (9)$$

When the ion is about to make a pore into the interface at x, it has to overcome the interfacial energy corresponding to the area of the pore, as shown in Fig. 3. Significance of the energy of the

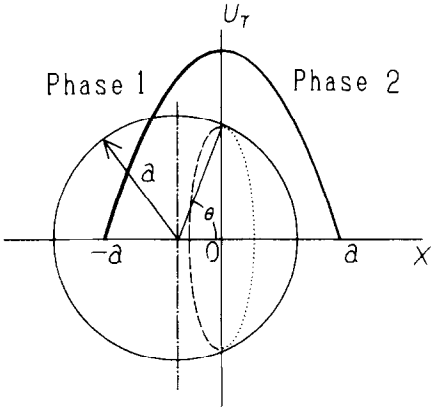

Fig. 3. The profile of the interfacial energy due to the surface tension.

pore formation has been introduced by Cunnane *et al.*[28]. Letting the surface energy or the surface tension between the two phases be γ, we obtain the symmetric energy profile:

$$U_\gamma = \pi(a \sin\theta)^2\gamma = \pi a^2\gamma(1 - x^2/a^2) \quad (10)$$

The sum of equations (4), (8) and (10) gives the energy profile for the forward transfer:

$$U_+ = \left\{2\alpha(\phi_2 - \phi_1)\frac{x}{w} + (1-\alpha)\phi_1 + \alpha\phi_2\right\}ze + 2\pi a^2\left(1 + \frac{x}{a}\right) \times (u_0 - u_1) + \pi a^2\gamma\left(1 - \frac{x^2}{a^2}\right) \quad (11)$$

and the maximum of $U_+ - ze\phi_1$ is the activation energy:

$$U_{A+} = \alpha ze(\phi_2 - \phi_1) + 2\pi a^2(u_0 - u_1) + \pi a^2\gamma \quad (12)$$

In contrast, the sum of equations (3), (9) and (10) is the activation energy for the backward transfer:

$$U_- = \left\{2(1-\alpha)(\phi_2 - \phi_1)\frac{x}{w} + (1-\alpha)\phi_1 + \alpha\phi_2\right\}ze + 2\pi a^2\left(1 - \frac{x}{a}\right) \times (u_0 - u_2) + \pi a^2\gamma\left(1 - \frac{x^2}{a^2}\right) \quad (13)$$

and the maximum of $U_- - ze\phi_2$ is

$$U_{A-} = -(1-\alpha)ze(\phi_2 - \phi_1) + 2\pi a^2(u_0 - u_2) + \pi a^2\gamma \quad (14)$$

The microscopic velocity of ions varies generally with thermal fluctuations, viscous force of the solvent and external forces such as the electric force and interfacial forces. The relation between the velocity and these forces can be expressed by the Langevin equation[23] or the Newton's law of motion associated with a random force. The Langevin equation has been applied to the formulation of ion current[29], in which the potential barrier is smoothed by the fluctuation. When an ion with mass m runs at v in a medium with viscous friction ξ subject to both the random force g and the external steady force f at x, the Langevin equation is given by

$$m\frac{dv(t)}{dt} + m\xi v(t) = f(x) + g(t) \quad (15)$$

Here ξ has a unit s^{-1} and is related with the coefficient of viscosity η (its SI unit being kg m^{-1} s^{-1})[30] through $m\xi = 6\pi a\eta$ for the spherical ion. Since ξ is a macroscopic value, it should be taken as an average value in both phases. The solution of equation (15) under the initial condition $v = v_0$ is expressed by[31]

$$v(t) = v_0\exp(-\xi t) + \frac{1}{m}\int_0^t \exp[-\xi(t-u)]\{f(x) + g(u)\}du \quad (16)$$

Since f is independent of the time, equation (16) is reduced to

$$v(t) = \frac{f}{m\xi} + \left(v_0 - \frac{f}{m\xi}\right)\exp(-\xi t) + v_F \quad (17)$$

where

$$v_F = \frac{1}{m}\int_0^t g(u)\exp[-\xi(t-u)]\,du \quad (18)$$

Since $g(t)$ is an assembly of randomly generated impulse functions with various positive or negative heights, v_F represents the fluctuating velocity. Only the positive component in v_F contributes to the forward transfer. We regard the time-average of the square root of the square-mean of v_F as the positive component. The derivation of the average is described in the Appendix because of a mathematical subject. Then the average is expressed by

$$\bar{v}_F^2 = \frac{k_B T}{m}\left\{1 + \frac{1}{2\xi t}[\exp(-2\xi t) - 1]\right\} \quad (19)$$

The observed current is a transfer rate averaged over the time which is much longer than a fluctuating period. Thus it is possible to take t to be infinity. From equations (17) and (19), we have the expression for the average velocity:

$$\bar{v} = \frac{f}{m\xi} + \sqrt{\frac{k_B T}{m}} \quad (20)$$

The forward transfer is accelerated by the force $f = -\partial U_+/\partial x$. From equations (11) and (20), the forward rate is given by

$$\vec{v}_+ = \sqrt{\frac{k_B T}{m}} + \frac{-2\pi a(u_0 - u_1) + 2\pi\gamma x - 2\alpha ze(\phi_2 - \phi_1)/w}{m\xi} \quad (21)$$

The velocity averaged over w, which is represented by the integral with respect to x in equation (1), is given by

$$\vec{v} = \sqrt{\frac{k_B T}{m}} + \frac{-2\pi a(u_0 - u_1 + \gamma/2) + 2\alpha\zeta k_B T/w}{m\xi} \quad (22)$$

where ζ is the dimensionless potential, defined by

$$\zeta = \frac{zF(\phi_1 - \phi_2)}{RT} \quad (23)$$

Since the force acting in the negative direction is $f = -\partial U_-/\partial(-x)$, the average backward rate is expressed by

$$\overleftarrow{v} = \sqrt{\frac{k_B T}{m}} - \frac{2\pi a(u_0 - u_2 + \gamma/2) + 2(1-\alpha)\zeta k_B T/w}{m\xi} \quad (24)$$

Equations (22) and (24) are independent of U, and hence equation (2) is valid. Then combination of equations (2), (12) and (14) yields

$$\vec{k} = \vec{v}\exp\left[\alpha\zeta - \frac{\{2(u_0 - u_1) + \gamma\}\pi a^2}{k_B T}\right] \quad (25)$$

$$\overleftarrow{k} = \overleftarrow{v}\exp\left[(\alpha - 1)\zeta - \frac{\{2(u_0 - u_2) + \gamma\}\pi a^2}{k_B T}\right] \quad (26)$$

Equations (22), (24)–(26) provide explicit forms of the transfer rates as a function of microscopic properties of the ion and the interface.

DISCUSSION

A net current is expressed by

$$j = zF(\vec{k}c_1 - \overleftarrow{k}c_2) \quad (27)$$

where c_i is the concentration of the ion in phase i ($i = 1, 2$) without mass transport. Letting concentrations under the equilibrium ($j = 0$) be c_1^* and c_2^*, equations (25)–(27) are reduced to

$$\frac{\vec{k}}{\overleftarrow{k}} = \frac{c_2^*}{c_1^*} = \frac{\vec{v}_{eq}}{\overleftarrow{v}_{eq}}\exp(\zeta_{eq} + \sigma_1 - \sigma_2) = \frac{1 + p\{2\alpha\zeta_{eq} - (w/a)(\sigma_0 - \sigma_1 + \kappa)\}}{1 + p\{2(\alpha - 1)\zeta_{eq} - (w/a)(\sigma_0 - \sigma_2 + \kappa)\}} \times \exp(\zeta_{eq} + \sigma_1 - \sigma_2) \quad (28)$$

where

$$p = \frac{\sqrt{k_B T}}{\sqrt{m}\xi w} \quad (29)$$

$$\sigma_i = \frac{2\pi a^2 u_i}{k_B T} \quad \text{for } i = 0, 1, 2 \quad (30)$$

$$\kappa = \frac{\pi a^2 \gamma}{k_B T} \quad (31)$$

The term of $\exp(\sigma_1 - \sigma_2)$ represents the difference in the solvation energies under the equilibrium. Thus the equilibrium potential shifts by $2\pi a^2(u_2 - u_1)/ze$[25]. Equation (28) deviates from the Nernst equation for any value of ζ_{eq} owing to $\vec{v} \neq \overleftarrow{v}$ or the differences in the electric force and solvation force of the two phases.

A question may arise as to why the equilibrium condition involves kinetic variables α and ξ. When the ion is accelerated or decelerated through the electric and the interfacial forces, it generates or consumes friction heats. The heat should be compensated thermodynamically with the electric potential and the entropy due to the concentration ratio. The compensating variable is p. Since $p^2 = k_B T/(m \cdot \xi^2 w \cdot w)$, it is the ratio of the thermal fluctuation energy to the frictional energy through the path w. An ideal interface is just a transmitter of substances, heat and energy without any change in itself. In this meaning, the present interface is not an ideal interface but may be regarded as a thin phase which alters thermodynamic variables. In other words, the equilibrium condition shown by equation (28) does not represent

an equilibrium between the two phases but the equilibrium among the three phases without heat balance.

For small values of p, the log-plot is approximately expressed by

$$\ln \frac{c_1^*}{c_2^*} \simeq (1 + 2p)\left(\frac{zF}{RT}\right)(\phi_1 - \phi_2)_{eq} + (\sigma_1 - \sigma_2)\left(1 + \frac{pw}{a}\right) \quad (32)$$

Since $p > 0$, the inverse slope $[RT/zF(1 + 2p)]$ is always smaller than $59.6/z$ mV at 25°C. It is assumed that the potential gradient occurs in the monomolecular bi-layer which sandwiches an imaginary sharp interface. For solvent molecules 0.1 nm in common diameter in both phases, we have $w = 0.2$ nm. When $\eta = 10^{-3}$ Pa s, $a = 0.1$ nm and $m = 0.1$ kg mol^{-1}, the value of $2p$ is 0.15, indicating a detectable value.

We define the potential independent rate as

$$k_0 = \sqrt{\frac{k_B T}{m}} \exp\left[-\frac{\pi a^2}{k_B T}(2u_0 - u_1 + u_2)\right] \quad (33)$$

Then the forward rate constant is rewritten as

$$\frac{\vec{k}}{k_0} = \left[1 + p\left\{2\alpha\zeta - \frac{(\sigma_0 - \sigma_1 + \kappa)w}{a}\right\}\right] \times \exp\left[\alpha\zeta + \frac{\sigma_1 - \sigma_2}{2}\right] \quad (34)$$

By the use of $\gamma = 0.025$ J m^{-2} for the water/nitrobenzene interface in equation (21), we find that the term of the interfacial tension $(\pi\gamma a/m\zeta)$ is only 3% of $\sqrt{k_B T/m}$. Thus κ can be neglected. Figure 4 shows variations of $\ln(\vec{k}/k_0)$ with ζ for some combinations of σ_0 and p, indicating almost linear dependence. The slope increases slightly with an increase in $\sigma_1 - \sigma_0$, $\sigma_2 - \sigma_0$ and p. Thus α evaluated from the Butler–Volmer equations is larger than the value from equation (34). For small values of p, it is approximated as

$$\ln\left(\frac{\vec{k}}{k_0}\right) \simeq \alpha\zeta(1 + 2p) + \frac{(\sigma_1 - \sigma_2)}{2} - \frac{p(\sigma_0 - \sigma_1)w}{a} \quad (35)$$

The linear variation of $\ln \vec{k}$ with ζ is obvious. The degree of the overestimation of α by the Butler-Volmer equation is at most $2p$. However, experimental values for some anions show concave variations (see the inset of Fig. 4). The deviation from the line is likely to be found for small (BF_4^-) and non-spherical (SCN^-) ions. Since a non-spherical ion has a dipole moment, it may be oriented by the strong electric field at the interface. Then the effective radius of the ion normal to x is less than the hydrodynamic radius a. Equations (33) and (35) predict that the decrease in a increases $\vec{k}$. Nevertheless, the forced orientation may distort the arrangement of solvent molecules which might occur at a spherical ion and hence enhance u_0 at the cost of the decreases in a. Consequently, $\vec{k}$ may decrease at the high overpotential.

The Goldman-type kinetic equation by Kakiuchi[18] is given by

$$\ln(\vec{k})_{Gldm} = \ln\left[\frac{(D/\Delta x)\zeta}{1 - e^{-\zeta}}\right] \simeq \ln\left(\frac{D}{\Delta x}\right) + \frac{\zeta}{2} \quad \text{for } \zeta \to 0 \quad (36)$$

Comparison of equation (36) with (35) shows the correspondence $k_0 \leftrightarrow D/\Delta x$ and $(1 + 2p)\alpha \leftrightarrow 1/2$. In the absence of the activation energy ($u_1 = u_0$ and $u_2 = u_0$), equation (33) shows that $k_0 = \sqrt{k_B T/m} = \sqrt{(m/2)(\bar{v})^2_{f=0}/m} = (\bar{v})_{f=0}/\sqrt{2} \leftrightarrow D/\Delta x$. This indicates that the thermal fluctuation causes the diffusion through the viscous layer Δx thick. In spite of the reasonable correspondence at $\zeta = 0$, the curve of $\ln(\vec{k})_{Gldm}$ vs. ζ is different from curves of equation (35), as shown in Fig. 4.

We define the exchange current density as

$$j_0 = zFk_0\left[1 + p\left\{2\alpha\zeta_{eq} + \frac{(\sigma_1 - \sigma_0 - \kappa)w}{a}\right\}\right] \times \exp\left[\alpha\zeta_{eq} + \frac{\sigma_1 - \sigma_2}{2}\right]$$
$$= zFk_0\left[1 + p\left\{2(1 - \alpha)\zeta_{eq} + \frac{(\sigma_2 - \sigma_0 - \kappa)w}{a}\right\}\right] \times \exp\left[(\alpha - 1)\zeta_{eq} + \frac{\sigma_2 - \sigma_1}{2}\right] \quad (37)$$

Then the current–potential curves are expressed by

$$\frac{j}{j_0} = \frac{1 + p\{2\alpha\zeta + (\sigma_1 - \sigma_0 - \kappa)w/a\}}{1 + p\{2\alpha\zeta_{eq} + (\sigma_1 - \sigma_0 - \kappa)w/a\}} \times \exp[\alpha(\zeta - \zeta_{eq})]\frac{c_1}{c_1^*} - \frac{1 + p\{2(\alpha - 1)\zeta + (\sigma_2 - \sigma_0 - \kappa)w/a\}}{1 + p\{2(\alpha - 1)\zeta_{eq} + (\sigma_2 - \sigma_0 - \kappa)w/a\}} \times \exp[(\alpha - 1)(\zeta - \zeta_{eq})]\frac{c_2}{c_2^*} \quad (38)$$

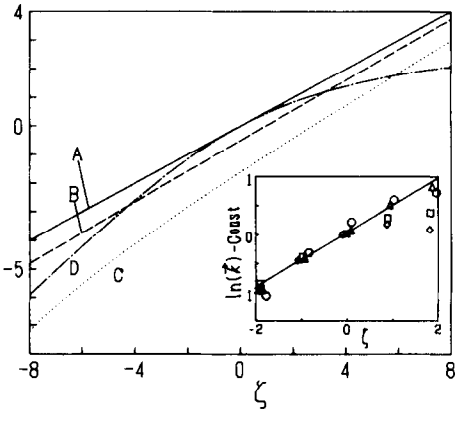

Fig. 4. Variation in $\ln \vec{k}/k_0$ with ζ calculated from equation (34) for (A) $p = 0$ (Butler–Volmer equation), (B) $\sigma_0 = 4$, $p = 0.02$, and (C) $\sigma_0 = 8$, $p = 0.02$ when $\sigma_1 = \sigma_2 = 0$, $\alpha = 0.5$ and $\kappa = 0$. Curve (D) is the Goldman-type equation by Kakiuchi. The plots of the inset are for SCN^- (◇), BF_4^- (□), $ClOF_4^-$ (△) and PF_6^- (○), cited from Fig. 3[20].

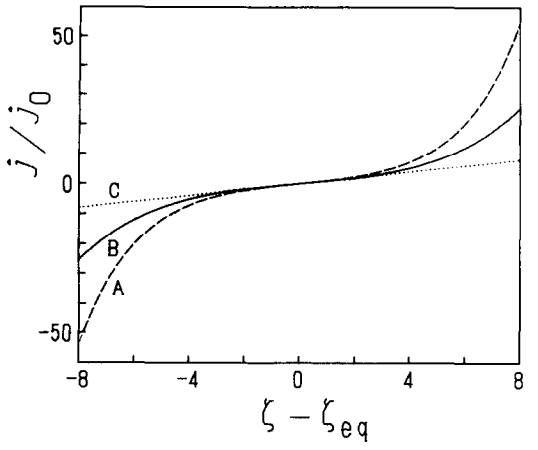

Fig. 5. Current–potential curves without concentration polarization computed from equation (38) for (A) $p = 0$ (Butler-Volmer equation), (B) $p = 0.04$ when $\sigma_0 = 8$, $\sigma_1 = \sigma_2 = 0$, $\zeta_{eq} = 0$ and $\alpha = 0.5$. Curve (C) is the Goldman type equation by Kakiuchi.

Figure 5 shows current–potential curves without concentration polarization. The current is larger than the current of the Butler–Volmer equation by ca. factor $1 + 2p$. It differs from the Kakiuchi's theory by 7% and 18%, respectively for $|\zeta/\zeta_{eq}| = 1$ (26 mV at 25°C) and 2.

We now consider the relation between the present theory and Butler–Volmer's kinetics or now Kakiuchi's theory. When the frictional energy is much larger than the fluctuation energy ($p \to 0$), the interfacial force and the electric force do not alter the velocity of the ion. Then the velocity retains in the bulk, and equation (38) becomes the Butler–Volmer equation. In order to cause the ion-transfer, the electric activation energy should overcome the non-electric activation. Conversely, as the frictional energy or p gets smaller, the interfacial forces facilitates the ion-transfer. When p is so large that the activation energy may be neglected, equation (38) is reduced to

$$j/j_0 \to \frac{2\alpha\zeta + (\sigma_1 - \sigma_0)w/a}{2\alpha\zeta_{eq} + (\sigma_1 - \sigma_0)w/a}\frac{c_1}{c_1^*} - \frac{2(\alpha - 1)\zeta + (\sigma_2 - \sigma_0)w/a}{2(\alpha - 1)\zeta_{eq} + (\sigma_2 - \sigma_0)w/a}\frac{c_2}{c_2^*} \quad (39)$$

The current–potential curve is linear with ζ. Especially for $\alpha = 0.5$ and $\sigma_1 = \sigma_2$, j/j_0 is linear to ζ with a slope of $c_1/c_1^* - c_2/c_2^*$. This is consistent with Kakiuchi's theory.

CONCLUSIONS

A key of the present theory is that physical properties of the double layer are reflected to the microscopic velocity of the ion, which controls the rate of the ion-transfer. The non-electric activation energies considered here were desolvation energy and the surface energy making a pore. A cause of the non-electronic energies is not significant in view of the viscous contribution so far as the energy is proportional to the surface area of the ion. Since the change in the velocity within the interface brings about energy loss, the equilibrium condition between the two phases results in containing kinetic variables in the Nernst equation. When the viscous effect is large or when the velocity in the bulk retains in the double layer ($p \to 0$), the kinetic equation is reduced to the Butler–Volmer equation. In contrast, when the viscous effect is so small that the velocity is subject to the interfacial force, the ion can traverse the interface without electric activation energy. Then the ion-transfer is caused by diffusion associated with the interfacial electric field. Therefore, the present theory covers the two limiting cases by simple assignment of p. Unfortunately, the theory does not explain quantitatively the concave variation of $\ln \vec{k}$ with ζ. The variation may be ascribed to alteration of desolvation by the electric field.

REFERENCES

1. H. H. Girault and D. J. Schiffrin in *Electroanalytical Chemistry* (Edited by A. J. Bard) Vol. 15, p. 1. Marcel Dekker, New York (1989).
2. M. Senda, T. Kakiuchi and T. Osaki, *Electrochim. Acta* **36,** 253 (1991).
3. Z. Samec, *J. Electroanal. Chem.* **99,** 197 (1979).
4. J. Koryta, *Ion-Selective Electrode Rev.* **5,** 131 (1983).
5. R. P. Buck and W. E. Bronner, *J. Electroanal. Chem.* **197,** 179 (1986).
6. H. H. Girault and D. J. Schiffrin, *J. Electroanal. Chem.* **197,** 213 (1985).
7. H. H. Girault, *J. Electroanal. Chem.* **200,** 3 (1986).
8. Y. Y. Gurevich and Y. I. Kharkats, *J. Electroanal. Chem.* **200,** 3 (1986).
9. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, pp. 92–97. John Wiley & Sons, New York (1980).
10. T. Osakai, T. Kakiuchi and M. Senda, *Bull. Chem. Soc. Jpn* **58,** 2626 (1985).
11. Z. Samec and V. Marecek, *J. Electroanal. Chem.* **200,** 17 (1986).
12. T. Wandlowski, V. Maracek and Z. Samec, *J. Electroanal. Chem.* **242,** 291 (1988).
13. T. Wandlowski, V. Marecek, K. Holub and Z. Samec, *J. Phys. Chem.* **93,** 8204 (1989).
14. T. Kakiuchi, J. Noguchi, M. Kotani and M. Senda, *J. Electroanal. Chem.* **296,** 517 (1990).
15. Y. Shau and H. H. Girault, *J. Electroanal. Chem.* **282,** 59 (1990).
16. Y. Shau, J. A. Campbell and H. H. Girault, *J. Electroanal. Chem.* **300,** 415 (1991).
17. P. G. Wolynes, *Ann. Rev. Phys. Chem.* **31,** 345 (1980).
18. T. Kakiuchi, *J. Electroanal. Chem.* **322,** 55 (1992).
19. T. Kakiuchi, J. Noguchi and M. Senda, *J. Electroanal. Chem.*, **336,** 137 (1992).
20. T. Kakiuchi, J. Noguchi and M. Senda, *J. Electroanal. Chem.* **327,** 63 (1992).
21. W. Nernst, *Z. Phys. Chem. Leipzig*, **2,** 613 (1888).
22. T. Osakai, T. Kakutani and M. Senda, *Bull. Chem. Soc. Jpn.* **57,** 370 (1984)
23. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics, International Series of Monographs on Physics 73*, p. 52. Oxford University Press, New York (1986).
24. V. S. Markin and A. G. Volkov, *Electrochim. Acta* **34,** 93 (1989).
25. K. Aoki, *J. Electroanal. Chem.* **386,** 17 (1995).
26. D. E. Goldman, *J. Gen. Physiol.* 27, 37 (1943).

27. I. Benjamin, *J. Chem. Phys.* **96,** 577 (1992).
28. V. J. Cunnane, D. J. Shiffrin, M. Fleischmann, G. Geblewicz and D. Williams, *J. Electroanal. Chem.* **243,** 455 (1988).
29. Yu. Y. Gurevich and Yu. I. Kharkats, *J. Electroanal. Chem.* **200,** 3 (1986).
30. P. W. Atkins, Physical Chemistry, fifth edition, p. 823. Oxford University Press, Oxford (1994).
31. K. Aoki and K. Hayashi, *J. Electroanal. Chem.* **384,** 33 (1995).

APPENDIX

The time-average of the square mean of v_F is evaluated in this appendix. It is defined by,

$$\bar{v}_F^2 = \frac{1}{t}\int_0^t v_F(z)^2\,dz \tag{40}$$

Inserting equation (18) into equation (40) and changing the order of the integration by the use of the Leipnitz's relation[32], we have

$$\begin{aligned}\bar{v}_F^2 &= \frac{1}{tm^2}\int_0^t\int_0^t g(z-u)\exp(-\xi u)\,du \\ &\quad\times\int_0^t g(z-x)\exp(-\xi x)\,dx\,dz \\ &= \frac{1}{tm^2}\int_0^t\int_0^t\int_{\min(u,x)}^t g(z-u)g(z-x) \\ &\quad\times\exp[-\xi(u+x)]\,dz\,du\,dx\end{aligned} \tag{41}$$

where $\min(u, x)$ denotes a minimum value of u or x. Function $g(u)$ is defined by the integral representation of the correlating function[23]:

$$\frac{1}{z}\int_0^z g(t_1-t)g(t-t_2)\,dt = 2m\xi k_B T\delta(t_1-t_2) \tag{42}$$

where δ is the delta function. Then equation (41) is reduced to

$$\begin{aligned}\bar{v}_F^2 &= \frac{1}{tm^2}\int_0^t\int_0^t [t-\min(u,x)]2m\xi k_B T\delta(u-x) \\ &\quad\times\exp[-\xi(u+x)]\,du\,dx \\ &= \frac{2\xi k_B T}{tm}\int_0^t (t-x)\exp(-2\xi x)\,dx\end{aligned} \tag{43}$$

The integration leads to equation (19).